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Trends in valence band electronic structure of mixed uranium oxides

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Valence band electronic structure of mixed uranium oxides (UO₂, U₃O₈, U₄O₉, U₃O₇, β-UO₃) has been studied by the resonant inelastic X-ray scattering (RIXS) technique at the U M₅ edge and by computational methods. We show here that the RIXS technique and recorded U 5f - O 2p charge transfer excitations can be used to proof the validity of theoretical approximations.

Structural, electronic and chemical properties of uranium (U) oxides vary strongly upon a transformation from the fluorite-type UO₂ structures to the layered structure of the higher U oxides (U₃O₇ and above)1-13. The mechanism of the expansion of the fluorite structure is reasonably straightforward14-16, however the role of oxygen (O) atoms in these structural changes remains less clear. We performed the state-of-art valence band RIXS experiment at the U M₅ edge for a number of binary U oxides – UO₂, U₃O₈, U₄O₉, U₃O₇, β-UO₃ – in order to clearly identify the mechanism causing the electronic structure modification upon oxidation of UO₂.

Valence band RIXS data at the U M₅ edge (~3550 eV) have been previously reported for UO₂, U₃O₈, UF₄, U₅O₈(NO₃)₂·6(H₂O) and several U intermetallic systems17-20, and have been proved to be sensitive to the structural environment of U atom and its ligands. Actually, the valence band RIXS data include the elastic and inelastic scattering profiles with an energy resolution of ~1eV.

Valence band RIXS data at the U M₅ edge (~3550 eV) have been previously reported for UO₂, U₃O₈, UF₄, U₅O₈(NO₃)₂·6(H₂O) and several U intermetallic systems17-20, and have been proved to be sensitive to the structural environment of U atom and its ligands. Actually, the valence band RIXS data include the elastic and inelastic scattering profiles with an energy resolution of ~1eV.

Fig. 1. Valence band RIXS spectra of UO₂, U₃O₇, U₄O₉, U₃O₈ and β-UO₃ recorded at the incident photon energy set to the maximum of the U M₅ edge. The experimental total energy resolution of ~1eV was achieved by employing Johann-type X-ray emission spectrometer with five spherically bend Si(220) crystal analyzers with 1m bending radius (see ESI for details).
scattering profile at emitted energies ~3545-3555 eV, reported in Fig.1 has been attributed to charge transfer process between U 5f states and O 2p states\textsuperscript{18–20}. The energy separation between elastic and inelastic scattering contributions to the spectra depends of the energy difference between the occupied O 2p states and unoccupied U 5f states.

Up to now it was expected that the occupied O 2p level stays at constant energy with respect to the Fermi level while the U 5f states move up in energy upon the changes of the oxidation state of U from U(IV) \(\rightarrow\) U(V) \(\rightarrow\) U(VI). Our recent studies of the evolution of the U chemical state in a series of U oxides confirms a changeover of the oxidation states U(IV) - U(V) - U(VI) through the charge compensation mechanisms\textsuperscript{5,19,22}. The established formal oxidation states for U in mixed U oxides are included in brackets: UO\(_2\)(IV), U\(_4\)O\(_9\)(IV-V), U\(_3\)O\(_7\)(IV-V), U\(_3\)O\(_8\)(V-VI), \(\beta\)-UO\(_3\)(VI). Moreover the exact quantitative analysis has been performed and showed the presence of 50% and 50% of U(IV) and U(V), respectively, in U\(_4\)O\(_9\), 33% and 67% of U(IV) and U(V) in U\(_3\)O\(_7\), and 67% and 33% of U(V) and U(VI) in U\(_3\)O\(_8\)\textsuperscript{5}.

Based on these findings the process of the electron transfer from the O 2p orbitals to the unfiled U 5f shell should show the constant increase of the energy separation between the elastic and inelastic scattering contributions in the spectra through the series of these mixed valence oxides. However, measured valence band RIXS data for the U oxides (Fig.1) show that the mechanism of the electronic structure modification during the transformation of UO\(_2\) into the mixed oxides is however more complicated. Charge transfer also takes place between U sites and additionally incorporated O\(^2^-\) ions in binary oxides. As a result, the modification of the U-ligand bonding induces a change in the U oxidation state. In addition to that, the position and distribution of valence band states near the Fermi level changes significantly on a scale of several eV.

To gain better understanding and to clarify the mechanism of charge transfer excitations and electronic structure modifications we performed three types of calculations with methods of computational quantum chemistry, which have been used to evaluate the properties of U oxides materials previously\textsuperscript{23–30}.

Computation of mixed U oxides is a challenging task because of a strongly correlated and localized character of the f electrons\textsuperscript{23,30}. The commonly used density functional (DFT) methods often fail even on the qualitative level, for instance predicting a metallic state for UO\(_2\)\textsuperscript{23}, which is in reality a Mott insulator with a wide band gap of 2.1 eV\textsuperscript{31}. To correct for this, the DFT+U method is often used when an on-site Coulomb interaction is modelled by an additional term in the Hamiltonian, whose strength depends on the Hubbard U parameter\textsuperscript{23,32,33}. This parameter in calculations for uranium oxides is usually taken as U=4.5 eV (with additional J parameter of 0.54eV) or an effective parameter, U\(_{eff}\) = U-J, is applied\textsuperscript{30,33}. These values come from the measurements of the correlation energy performed on UO\(_2\)\textsuperscript{34,35}. This approximation is the most common approach in the calculations of the electronic structure of U systems\textsuperscript{10,19,23,25,29,36,37}.

Recently, Beridze and Kowalski\textsuperscript{23,30} performed systematic tests of the performance of the DFT+U method with the Hubbard U parameter derived \textit{ab initio} using the linear response method of Cococcioni and Gironcoli\textsuperscript{33} for the calculations of actinide bearing molecular and solid compounds, including U oxides. They have shown that the Hubbard U parameter values strongly depend on the oxidation state of U, being largest for U(VI) (~3 eV) and smallest for U(IV) (~2 eV). In follow up studies a similar trend has been shown for other actinides\textsuperscript{38}. Here we test the performance of this methodology for the computation of the electronic density of states (DOS) that are used for the construction of theoretical RIXS data.

In most of the DFT+U implementations the shape of the orbitals of interest (f orbitals in the case of U) have to be provided in order to estimate the occupation of these orbitals and compute the Hubbard energy correction term\textsuperscript{29,33}. These orbitals are usually represented by the atomic orbitals computed for atoms or ions and thus not necessarily adequately represent the shape of the orbital in a solid. In recent studies the maximally localized Wannier functions have been applied in computation of electronic structure of solids\textsuperscript{32,38–40}. In this contribution we will test this approach in order to check if the Wannier functions-based representation of f orbitals can result

![Fig. 2. Comparison of measured valence band RIXS spectra of UO\(_2\), U\(_3\)O\(_7\), U\(_3\)O\(_8\) and \(\beta\)-UO\(_3\) and results of calculations using a variety of methods, denoted as standard approach with U =4.5eV and J=0.54eV (M1), atomic orbitals (M2), Wannier Functions (M3).](image)
in any significant improvement in the description of the DOS functions and RIXS data.

In order to reproduce the experimentally detected charge transfer excitations we made simplified calculations by inserting the calculated partial U 5f and O 2p DOSs into the Kramers-Heisenberg equation\(^{16,42}\). This approach provides straight forward information about the validity or accuracy of DOSs calculated using a variety of methods. It describes a correlation between occupied and unoccupied states under assumption that the hybridization between U 5f and O 2p states takes place. In that case, the energy difference between the maxima of the occupied O 2p DOS and unoccupied U 5f DOS will define the energy transfer values for the observed RIXS transitions.

The partial DOSs have been calculated by three approaches (see ESI). First we have applied the most common approach assuming the standard values used in calculations for U oxides (U=4.5eV and J=0.54eV\(^2\)) (denoted as M1). In addition we computed the Hubbard U parameters values using the linear response method of Cococci and Gironcoli \(^{33}\). Here, for the calculations of the Hubbard correction we represent f orbitals for projection of occupations by the atomic orbitals (M2) and the Wannier functions (M3).

Computation of the electronic structure of U oxides can often lead to the convergence to a metastate instead of ground state\(^{27}\). In order to obtain the correct electronic structure of the considered oxides, for an initial electronic state we computed the expected charges of the different U atoms in the mixed U oxides using bond valence sum (BVS) method\(^{42}\). The BVS of U atoms for the considered oxides: U\(_2\)O\(_7\) (P4\(_2\)/n\(^{13}\)), U\(_3\)O\(_8\) (Ammm), UO\(_2\) (P12\(_1\)11), and UO\(_2\) (Fm-3m) were calculated and analyzed applying the following formula:

$$V = \sum \exp \left( \frac{R_i - a_i}{b} \right) $$

Here the bond valence parameter \(R_i\) and constant \(b\) are taken from Ref.\(^{43}\) and \(d_i\) are the corresponding valence and bond lengths for each phase. The BVS results are given in ESI, where the U average charge is in approximate agreement with our previous findings\(^{5,22}\).

The Hubbard U parameter values computed with the linear response for the considered U oxides are given in Table 1. In general, as in our previous studies\(^{30}\), the value is smaller than 4.5 eV, but strong dependence on the oxidation state is observed. The largest value was obtained for UO\(_3\) (U(VI)) and the smallest for UO\(_2\) (U(IV)).

Table 1: The computed Hubbard U parameter values in eV

<table>
<thead>
<tr>
<th></th>
<th>U(V)</th>
<th>U(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO(_2)</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>U(_2)O(_7)</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>U(_3)O(_8)</td>
<td>2.0</td>
<td>2.2</td>
</tr>
<tr>
<td>β-UO(_3)</td>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Predicted and measured band gaps (in eV) of the mixed U oxides

<table>
<thead>
<tr>
<th></th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO(_2)</td>
<td>2.4</td>
<td>0.3</td>
<td>0.7</td>
<td>2.1</td>
</tr>
<tr>
<td>U(_2)O(_7)</td>
<td>1.4</td>
<td>0.6</td>
<td>0.9</td>
<td>1.6</td>
</tr>
<tr>
<td>U(_3)O(_8)</td>
<td>1.7</td>
<td>0.9</td>
<td>1.3</td>
<td>1.8</td>
</tr>
<tr>
<td>β-UO(_3)</td>
<td>2.2</td>
<td>2.0</td>
<td>2.7</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Table 3: The computed and measured energy difference between U 5f and O 2p states. The energies are given in eV

<table>
<thead>
<tr>
<th></th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO(_2)</td>
<td>6.5</td>
<td>6.3</td>
<td>7.0</td>
<td>7.5</td>
</tr>
<tr>
<td>U(_2)O(_7)</td>
<td>5.8</td>
<td>5.6</td>
<td>6.5</td>
<td>5.5</td>
</tr>
<tr>
<td>U(_3)O(_8)</td>
<td>5.2</td>
<td>5.3</td>
<td>6.1</td>
<td>6.0</td>
</tr>
<tr>
<td>β-UO(_3)</td>
<td>5.2</td>
<td>5.5</td>
<td>6.5</td>
<td>6.2</td>
</tr>
</tbody>
</table>

The issue of the DFT or DFT+U predicted band gaps has been discussed previously\(^{10}\). One interesting aspect in the case of UO\(_2\), which is often used as a model system, is that for the Mott insulator the band gap value should be well approximated by the value of the Hubbard U parameter. The measured band gap for UO\(_2\) is 2.1 eV, which is close to the Hubbard U parameter value predicted by the linear response method (Table 1). The problem as outlined by Breridge and Kowalski\(^{10}\) is that the atomic orbitals used to represent the f orbitals in solids are not a good representation resulting in a significant and unrealistic fractional occupation of the unoccupied f levels (up to 0.3 for UO\(_2\)). In order to remove this obstacle we applied the Wannier representations of the f orbitals for the DFT+U calculations, which resulted in more realistic, close to zero occupations of the unoccupied f orbitals. The RIXS profiles resulting from the later calculations are also plotted in Fig. 2. These represent the best match to the measured RIXS profiles with good prediction of the position of the U 5f - O 2p charge transfer and an overall much better match to the observed shape of the U 5f - O 2p charge transfer excitations.
band RIXS - one can improve the theoretical prediction of the DOSs of actinide contained materials.

Conflicts of interest
There are no conflicts to declare.

Notes and references
P.M.K. and J.L. thank the JARA-HPC for giving time on the supercomputing resources awarded through JARA-HPC Partition. S.M.B. acknowledges support from the Swedish Research Council (research grant 2017-06465) and K.O.K acknowledges support from ERC (research grant 759696).

Electronic Supplementary Information

1. Experimental Methods

The measurements were performed at beamline ID26\textsuperscript{1,2} of the European Synchrotron (ESRF) in Grenoble. The incident energy was selected using the <111> reflection from a double Si crystal monochromator. Rejection of higher harmonics was achieved by three Si mirrors at an angles of 3.0, 3.5 and 4.0 mrad relative to the incident beam. Resonant inelastic X-ray scattering (RIXS) at the U M\textsubscript{5} edge was measured by scanning the emission energy at the fixed incident energy using an X-ray emission spectrometer. The sample, analyzer crystal and photon detector (silicon drift diode) were arranged in a vertical Rowland geometry. The emission energy was selected using the <220> reflection of five spherically bent Si crystal analyzers (with 1m bending radius) aligned at the 65° Bragg angle. The paths of the incident and emitted X-rays through air were minimized in order to avoid losses in intensity due to absorption. The intensity was normalised to the incident flux. A combined (incident convoluted with emitted) energy resolution of 1.0 eV was obtained as determined by measuring the full width at half maximum (FWHM) of the elastic peak.

All samples were prepared from depleted nuclear grade UO\textsubscript{2+x} supplied by FBFC International (Dessel, Belgium). An assessment of the impurity content of this powder has been reported elsewhere.\textsuperscript{3} Conditions for preparation of the various samples were evaluated via simultaneous thermal analysis (Netzsch STA 449 F1 Jupiter). The preparation of UO\textsubscript{2.0}, U\textsubscript{4}O\textsubscript{9}, and U\textsubscript{3}O\textsubscript{7} has been described in detail in Refs. 4 and 5\textsuperscript{4,5}. U\textsubscript{3}O\textsubscript{8} powder was synthesized by oxidation of as-received UO\textsubscript{2+x} powder at 500°C or 4 h under a constant flow of dry air (N\textsubscript{2} / 21 vol.% O\textsubscript{2}). A wet - chemical route was employed to produce β-UO\textsubscript{3}. As-received UO\textsubscript{2+x} powder was first dissolved in nitric acid and subsequently titrated with an excess of an ammonia aqueous solution, which results in precipitation of ammonium diuranate (ADU). β-UO\textsubscript{3} was then obtained by calcining the ADU powder at 550°C for 30 min. Phase purity of all samples was confirmed via X - ray diffraction. Powders (30-50 mg) were intimately mixed with boron nitride powder and compacted into thin pellets. These pellets were placed in sample holders dedicated to cryostat operation at beamline ID26 and sealed with Kapton foil.

2. Theoretical Calculations

Valence band RIXS calculations at the U M\textsubscript{5} edge were performed by inserting the U 5f and O 2p density of states into the Kramers-Heisenberg equation\textsuperscript{6}:

\[ F(\Omega, \omega) = \int_{\epsilon} d\epsilon \frac{\rho(\epsilon)\rho'(\epsilon + \Omega - \omega)}{(\epsilon - \omega)^2 + \frac{\Gamma_n^2}{4}} \]  \hspace{1cm} (1)

Where \( \rho \) and \( \rho' \) are the density of occupied and unoccupied U f and O p states, while \( \Omega \) and \( \omega \) represent the energies of the incident and scattered photons, respectively. \( \Gamma_n \) represents the lifetime broadening of the U 3d state, which is 3.8 eV\textsuperscript{7}. The validity of this approximation
has been already evaluated previously by comparison between experimental and theoretical results\textsuperscript{8-12}.

3. Computed density of states

The calculations were performed using DFT-based Quantum-ESPRESSO simulations package\textsuperscript{13}. The computational setup resembles the one used by Beridze and Kowalski\textsuperscript{14}. We applied the plane-wave cut off of 50 Ryd and ultra soft pseudopotentials to mimic the presence of core-electrons\textsuperscript{15}. In order to capture correctly the strongly correlated \( f \) electrons, following our previous studies of Uranium-bearing systems\textsuperscript{14}, we applied the DFT+\( U \) method\textsuperscript{16-18}. We have used the PBE sol exchange correlation functional\textsuperscript{19}. This is because it represents a small modification of the widely used PBE exchange-correlation functional\textsuperscript{20}, which better reproduces the slowly varying electronic density limit. It results in much better predictions of structural parameters, which is important for the purpose of our research. Nevertheless, there is no significant difference in the performance of the two mentioned functionals for computation of the electronic structures of uranium oxides\textsuperscript{14}.

For the computation of DOSs we used two approaches. In the first we have applied the standard approach assuming the standard values used in computation of Uranium-systems (\( U=4.5\text{eV} \) and \( J=0.54\text{eV} \))\textsuperscript{16} (named \textbf{M1}). In addition we computed the Hubbard \( U \) parameters values using the linear response method of Cococcioni & Gironcoli\textsuperscript{18}. Here, for the purpose of calculations of the Hubbard correction we represent \( f \) orbitals for projection of occupations with the atomic orbitals \textbf{(M2)} and the Wannier functions \textbf{(M3)}.

The initial atomic structures of the simulated oxides came from \( \text{UO}_2 \)\textsuperscript{21}, \( \beta-\text{UO}_3 \)\textsuperscript{22}, \( \text{U}_2\text{O}_8 \)\textsuperscript{23} and \( \text{U}_3\text{O}_7 \)\textsuperscript{24}. We have applied the Methfessel–Paxton k-points grids\textsuperscript{25}: 4x4x4 for \( \text{UO}_2 \), 2x2x6 for \( \text{UO}_3 \) and 3x2x5 for \( \text{U}_2\text{O}_8 \). \( \text{U}_3\text{O}_7 \) has been modelled by a large supercell containing 200 atoms and have been computed on the gamma point only. The lattice parameters have been optimized to the equilibrium values assuming \( P=\text{0 GPa} \) with the tolerance of \( 0.1 \\text{ GPa} \). The equilibrium was reached assuming the maximal residual force acting on atoms being smaller than \( \text{0.005 eV/Å} \).

Computation of the electronic structure of uranium-oxides is not a trivial task and can often lead to the convergence to a metastate\textsuperscript{26}. In order to obtain the correct electronic structure of the considered oxides, for an initial electronic state we computed the expected charges of the different uranium atoms in the considered mixed oxides using bond valence sum (BVS) method\textsuperscript{27}. The BVS of \( U \) atoms for the considered oxides: \( \text{U}_3\text{O}_7 \) (\textit{P4}_2/n\textit{Z}(86)), \( \text{U}_3\text{O}_8 \) (\textit{Amm2}), \( \text{UO}_3 \) (\textit{P1211}), and \( \text{UO}_2 \) (\textit{Fm}-3\textit{m}) were calculated and analyzed applying the following formula:

\[
V = \sum_i \exp \left[ \left( \frac{R_i - d_i}{b} \right) \right]
\]

Here the bond valence parameter \( R \) and constant \( b \) are taken from Ref\textsuperscript{28}. \( V \) and \( d_i \) are the corresponding valence and bond lengths for each phase. The BVS results of \( U \) atom for the title phases are given in \textbf{Table 1} and for the \( \text{U}_3\text{O}_7 \) phase illustrated in Figure 5. The obtained ab-initio charges for \( \text{U3O8} \) are (VI) and (V) for \( \text{U}(1) \) and \( \text{U}(2) \), respectively.
Table 1. Results of bond valence calculation for U₃O₈ (P4mm2), UO₃ (P1211), and UO₂ (Fm-3m), respectively.

<table>
<thead>
<tr>
<th>Phases</th>
<th>U–O bond lengths</th>
<th>Valence Sum (v.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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</tr>
<tr>
<td>U₃O₈ (P4mm2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>U(1)</td>
<td>2.074 ² 2</td>
<td>2.445</td>
</tr>
<tr>
<td>U(2)</td>
<td>2.074 ² 2</td>
<td>2.2068</td>
</tr>
<tr>
<td>UO₃ (P1211)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>U(1)</td>
<td>2.0711</td>
<td>2.2061</td>
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<td>U(2)</td>
<td>2.7234</td>
<td>2.3959</td>
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<td>U(3)</td>
<td>2.1701</td>
<td>1.7924</td>
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<td>U(4)</td>
<td>2.2388</td>
<td>2.1968</td>
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<tr>
<td>U(5)</td>
<td>2.7433</td>
<td>2.1142</td>
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<tr>
<td>UO₂ (Pm-3m)</td>
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</tr>
<tr>
<td>U(1)</td>
<td>2.3677</td>
<td>2.3677</td>
</tr>
</tbody>
</table>

Figure 1 - 4 shows partial Density of States (DOS) obtained by different theoretical methods.
Figure 1. Density of states curves for UO$_2$
Figure 2. Density of states curves for $\beta$-UO$_3$
Figure 3. Density of states curves for U₃O₈
Figure 4. Density of states curves for $\text{U}_3\text{O}_7$
Figure 5. The DFT+U and BVS charges on U atoms in U₃O₇ structure.

References: